



# Conversion of methyl mercaptan and methanol to hydrocarbons over solid acid catalysts – A comparative study



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## ABSTRACT

This study demonstrates that CH<sub>3</sub>SH (a harmful impurity in natural gas) can be selectively converted into H<sub>2</sub>S and hydrocarbons (M2TH process) on H-zeolite/zeotype with diverse topologies. The catalytic activity varied as follows: H-ZSM-5 > H-Y > H-FER > H-BEA > H-MOR > H-SAPO-34. In addition, H-ZSM-5 was the most stable catalyst toward deactivation by coke. The effect of the carrier gas (nitrogen or methane) and the role of water on the catalytic behavior of zeolites were explored under different conditions. Similar performances were obtained using CH<sub>3</sub>SH/N<sub>2</sub> or CH<sub>3</sub>SH/CH<sub>4</sub> mixtures, but the amount of coke drastically decreased and the catalyst lifetime increased when 2% of water was added into the reaction. M2TH was compared with the well-known MTH (methanol to hydrocarbons) process. Although there are similarities between the two processes, significant differences were also observed, essentially regarding the products formed and distributed. These aspects are discussed taking into account the reaction pathway involved in each process.

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## 1. Introduction

Mercaptans are harmful impurities found in natural gas. For environmental and industrial reasons, their concentration in natural gas needs to be kept below 5 ppmv [1]. Chemical processes used to remove them may include oxidation, alkaline treatment, reaction with olefins and hydro-desulfurization [2–5]. These all call for additional reagents, some of which produce dialkylsulfides or disulfides. The challenge lies in developing new methods, without adding any reactants (O<sub>2</sub>, H<sub>2</sub>, olefins, etc.), and in keeping waste production low.

We have recently shown that CH<sub>3</sub>SH (a very refractory compound in the gas clean-up processes) can be selectively transformed into hydrocarbons and H<sub>2</sub>S over protonic zeolites (H-ZSM-5, H-Y and H-Ferrierite), at 823 K [6]. H<sub>2</sub>S, as we know, can be efficiently captured by absorption using conventional solvents such as amines, and made commercially saleable through the Claus process. The chemical transformation of CH<sub>3</sub>SH is called M2TH (methyl mercaptan to hydrocarbons). Only very few data and no substantial discussion relating to the catalytic conversion of

methylmercaptan can be found in open literature [7–10]. Chang and Silvestri [7] reported that at 755 K, using H-ZSM-5 as catalyst, CH<sub>3</sub>SH was converted into H<sub>2</sub>S and hydrocarbons, but the desulfurization was only partial, with 27.2% of the feed carbon converted to dimethylsulfide (DMS). Butter et al. [8] claimed high CH<sub>3</sub>SH conversion to CH<sub>4</sub> at 550 °F (~531 K) on H-ZSM-5. Wachs [9] claimed near full CH<sub>3</sub>SH conversion to CH<sub>4</sub> and coke on H-SAPO-34 at 873 K. Mashkina et al. [10] identified the presence of CH<sub>4</sub> when CH<sub>3</sub>SH was processed on various acid catalysts between 623 and 673 K, while at lower temperatures, DMS was the only product, at equilibrium conversion.

In our previous study, the catalytic conversion of CH<sub>3</sub>SH was performed in a gas flow reactor using dinitrogen as carrier gas [6]. However, in a real process for removing CH<sub>3</sub>SH from natural gas, the gas used for stripping the pre-adsorption bed will preferably be wet methane. The present work therefore set out to study CH<sub>3</sub>SH conversion on H-zeolites in feeds of various compositions: N<sub>2</sub>, CH<sub>4</sub> and/or H<sub>2</sub>O. More zeolite/zeotype topologies were also screened in this study.

As a general comment, the M2TH process may have some similarities with the well-known MTH (methanol to hydrocarbon) process. The two processes were therefore run under equivalent conditions, using H-ZSM-5 zeolite as catalyst, to compare them.

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## 2. Experimental

### 2.1. Catalysts and chemicals

Commercial zeolites NH<sub>4</sub>-ZSM-5 (CBV 3024E; Si/Al = 15), H-Y (CBV 720; dealuminated Y faujasite with Si/Al ratio of 15), NH<sub>4</sub>-BEA (CP814E; Si/Al = 12.5), NH<sub>4</sub>-FER (CP914C; Si/Al = 10) and NH<sub>4</sub>-MOR (CBV21A; Si/Al = 10) were obtained from Zeolyst International. H-SAPO-34 and H-ZSM-5 (Si/Al = 75) were obtained from TOTAL SA. The catalytic materials were pressed, crushed and sieved to obtain an even grain size of 100–150  $\mu\text{m}$ . Before the catalytic testing, they were calcined in air for 5 h at 823 K to obtain their active hydrogen form. Tanks of N<sub>2</sub>, CH<sub>4</sub> and CH<sub>3</sub>SH/N<sub>2</sub> (5.0/95.0, v/v) were supplied by Air Liquide.

### 2.2. Characterization

XRD diffractograms of the zeolites were recorded on a Bruker D8 advance instrument with a copper X-ray source at a voltage of 40 kV and amperage of 40 mA. The system was upgraded with a Lynx Eye detector. All zeolite samples exhibited good crystallinity and the characteristic pattern of their structure.

The porous structure of the catalytic materials was studied by N<sub>2</sub> sorption, at 77 K with a Micromeritics ASAP 2010 sorptometer. Before analysis, the samples were desorbed in a vacuum at 573 K for 10 h. The apparent surface area (determined by applying the BET equation) and micropore volume were determined from the N<sub>2</sub> isotherm.

The acidity of the zeolites was evaluated by temperature-programmed desorption (TPD) of ammonia using an AUTOCHEM 2910 (Micromeritics) as per the method previously described [6]. The profiles of NH<sub>3</sub> desorption are shown in Fig. S1 (supplementary information).

To characterize the coke deposit on the catalyst, the microreactor was flushed with nitrogen at 823 K at the end of the reaction, in order to desorb any adsorbed species on the surface of the catalyst. 20 mg of the spent catalyst were then analyzed by thermogravimetry (TGA) with a NETZSCH TG 209C analyzer. The temperature program started with an isothermal period of 5 min at 298 K, and continued with a temperature ramp-up to 1173 K at 5 K min<sup>-1</sup> in air (Fig. S2, supplementary information). The weight loss between 723 and 1023 K was considered attributable to the burning of coke.

### 2.3. Catalytic tests

The catalytic conversion of CH<sub>3</sub>SH in various feed compositions was carried out in a stainless steel fixed-bed microreactor (4 mm i.d.) at atmospheric pressure. The composition of the reactor feed was adjusted with flow meters, using the following gases: CH<sub>3</sub>SH/N<sub>2</sub> (0.5/95.5, v/v), CH<sub>4</sub> and N<sub>2</sub>. H<sub>2</sub>O was introduced by saturation of CH<sub>4</sub> or N<sub>2</sub> flow. Standard experiments were performed with a bed of 100 mg catalyst supported by glass wool, using 5000 ppm CH<sub>3</sub>SH in various feeds (total flow: 50 mL min<sup>-1</sup>), at weight hourly space velocities (WHSV,  $\text{mass}_{\text{CH}_3\text{SH}}/\text{mass}_{\text{catalyst}} \text{ h}$ ) of 0.32 h<sup>-1</sup>. The products were analyzed online by gas chromatography, using a dual detector device, a flame ionization detector and a flame photometric detector [6].

The methanol was converted in a stainless steel fixed-bed reactor (i.d. 5 mm), using 250 mg of catalyst and nitrogen as carrier gas. Methanol (from Sigma-Aldrich) was supplied by means of an HPLC pump followed by evaporation in a nitrogen stream (WHSV = 0.3 h<sup>-1</sup>). The complete reactor effluent was analyzed by an online GC-FID system (Varian CP-3800), using a CP-PoraPLOT Q capillary column (27.5 m, 0.53 mm, 20  $\mu\text{m}$ ).

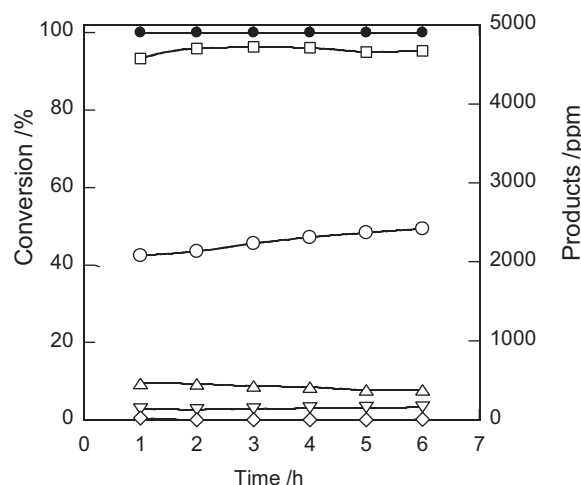


Fig. 1. Conversion of methylmercaptan vs. time on H-ZSM-5 at 823 K; (●) conversion, (□) H<sub>2</sub>S, (◇) DMS, (○) CH<sub>4</sub>, (▽) C<sub>2</sub>H<sub>6</sub>, and (△) BTX.

## 3. Results

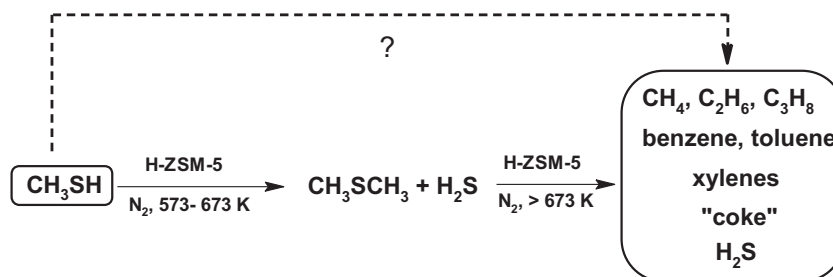
Experiments carried out in TPSR mode [6], using CH<sub>3</sub>SH or DMS as reagents, returned very useful results, which can be summarized as follows. From 573 to 673 K, the CH<sub>3</sub>SH conversion is 70–75% and the products consist of comparable amounts of CH<sub>3</sub>SCH<sub>3</sub> and H<sub>2</sub>S. Above 673 K, the CH<sub>3</sub>SH conversion increases, to reach nearly 100% at 823 K. The amount of DMS gradually decreases in favor of H<sub>2</sub>S, methane, ethane and propane (C1–C3), as well as benzene, toluene and xylene (BTX). Methane represents more than 90 vol% in C1–C3. At 823 K, there is no more DMS. Any traces of CH<sub>3</sub>SSCH<sub>3</sub> or CS<sub>2</sub> were not detected. When DMS was used as reagent, in the presence of H-ZSM-5, low conversion was observed below 723 K [6]. Beyond that temperature, DMS conversion increases very fast, and C1–C3, BTX and H<sub>2</sub>S are formed, confirming that DMS is an intermediate in M2TH. At 823 K, DMS is fully converted into H<sub>2</sub>S and hydrocarbons. Based on these results, a simple reaction pathway for the transformation of CH<sub>3</sub>SH on protonic zeolite at high temperature is suggested in Scheme 1.

For a better understanding of the M2TH process, and a valuable comparison of the various zeolite catalysts, a first set of isothermal experiments were carried out at 823 K for 6 h. Fig. 1 shows the example of CH<sub>3</sub>SH transformation on H-ZSM-5. At 823 K, a CH<sub>3</sub>SH conversion of ca. 99–100% is maintained for 6 h. The only carbon-containing products appearing in the gas phase are C1–C3 and BTX. As previously established [6], carbonaceous deposits (denominated coke) were formed on zeolite surfaces during the M2HT process. Therefore, the amount of coke produced on the catalysts after 6 h of reaction was evaluated by TGA and the TGA profiles between 773 and 973 K are shown in Fig. S2 (supplementary information).

Table 2 summarizes the catalytic behavior of various zeolites in the CH<sub>3</sub>SH conversion. The concentrations of DMS, C1–C3 and BTX are values averaged over the 6-h time-on-stream (tos). The average values of the conversions were estimated as  $\sum X_i/6$  ( $i = 1-6$ ), where  $X_i$  is the mercaptan conversion after  $i$  hours of tos. Similarly, the average values for the concentrations (C) were calculated as  $\sum C_i/6$  ( $i = 1-6$ ).

These data call for several comments:

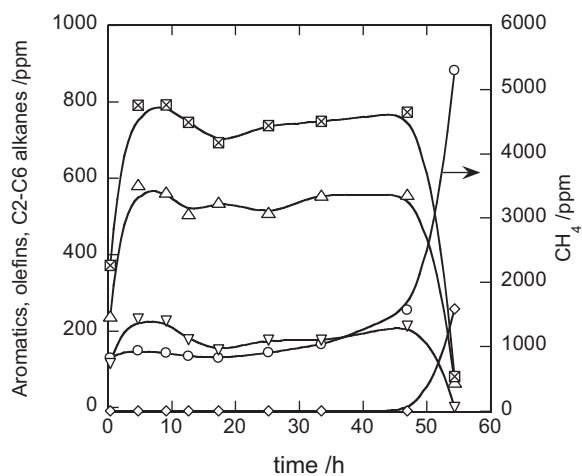
- (1) H-ZSM-5 is clearly the most active catalyst, achieving almost full conversion over the 6-h period, and releasing no DMS. It is also the most stable catalyst, which produced the least coke.



**Scheme 1.** Pathway of the catalytic transformation of  $\text{CH}_3\text{SH}$  into hydrocarbons on HZSM-5.

- (2) H-SAPO-34 and H-MOR exhibit the lowest activity, with a total  $\text{CH}_3\text{SH}$  conversion at about 75%. The DMS concentration in the final product is more than 1000 ppmv for both catalysts.
- (3) H-Y, H-Ferrierite and H-BEA exhibit an intermediate behavior, with 83–90%  $\text{CH}_3\text{SH}$  conversion, and a high amount of  $\text{CH}_3\text{SH}$  converted into hydrocarbons. Note that the largest amount of coke (15 mg) is formed on H-BEA.
- (4) Whatever the catalyst, DMS and  $\text{H}_2\text{S}$  are the only sulfur-containing products identified. The sulfur balance was in the range of 94–100%. Among the carbon-containing products, only C1–C3 alkanes and BTX were identified, and no olefins. It is important to note that the quantity of aromatics produced with H-ZSM-5 (about 50% in equivalent  $\text{CH}_4$ ) is far higher than with other zeolites. Assuming that all the weight loss from TGA is due to the burning of carbon in the catalyst, the carbon balance was in the range of 95–105%.

Based on the above comments, we can state that M2TH proves to have a number of points in common with the MTH process: methanol  $\rightarrow$  dimethylether  $\rightarrow$  hydrocarbons. In MTH, H-ZSM-5 is also the most active and stable catalyst, yielding the most aromatics and depositing the least coke [11–15]. However, olefins are the dominant aliphatic species in MTH, whereas only alkanes are formed in M2TH. It should be remembered, however, that MTH is typically run at 670–720 K, when M2TH was carried out at 823 K. These differences in product distribution between MTH and M2TH may find their explanation in the different reaction conditions. In order to clarify this point, we ran a methanol conversion at 823 K, in the presence of H-ZSM-5 ( $\text{CH}_3\text{OH}/\text{N}_2 = 0.8/99.2$ ;  $\text{WHSV} = 0.30 \text{ h}^{-1}$ ). Fig. 2 shows the evolution of methanol conversion and product concentrations as a function of time. As can be observed, the catalyst



**Fig. 2.** Conversion of methanol vs. time on H-ZSM-5 at 823 K; (○)  $\text{CH}_4$ , (×) olefins (ethene + propene), (▽) C<sub>2</sub>–C<sub>6</sub> alkanes, (△) aromatics (equivalent C<sub>8</sub>), and (◇) dimethylether.

exhibits very high stability. For the first 45 h, methanol is fully converted into hydrocarbons, mainly lower olefins and aromatics. As soon as dimethylether appears, after 45 h on stream, the formation of methane rises very fast at the expense of all other products.

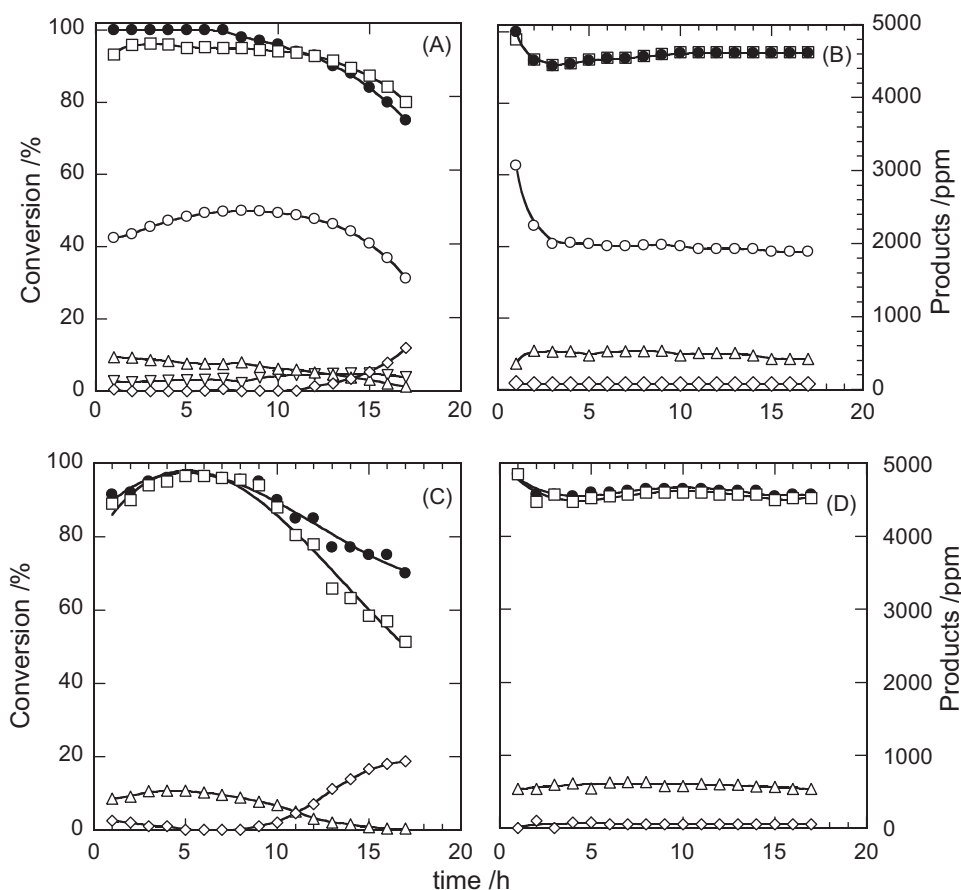
In a real application, the M2TH process will transform the  $\text{CH}_3\text{SH}$  in methane, after a possible pre-concentration step. Moreover, natural gas always contains a certain amount of water. For that reason, we ran a second round of experiments using various mixtures of  $\text{CH}_3\text{SH}$ ,  $\text{CH}_4$  and water. We chose H-ZSM-5 (the most stable catalyst) and the experiments were performed at 823 K over 17 h to see. In a blank experiment, only insignificant conversion of  $\text{CH}_4$  was observed at this temperature on H-ZSM-5. Fig. 3 shows the catalyst behavior for various feed compositions. The carbonaceous deposit in the spent catalysts was quantified by chemical analysis (C and S) and TGA. There is a good match between the weight loss (TGA) and the sum C + S (Table 3).

When  $\text{CH}_3\text{SH}$  is processed in the presence of  $\text{N}_2$  alone, the conversion rate remains at 99% for 8 h (Fig. 3A) before decreasing smoothly to 75% after 17 h of operation. After 10 h of reaction, DMS appears in the effluent. It is obvious from Fig. 3B, C and D that the catalytic behavior changed when the reaction feed contained water and/or methane. Catalyst deactivation is therefore faster for the  $\text{CH}_3\text{SH}/\text{CH}_4/\text{N}_2$  feed (Fig. 3C), but the presence of water makes the catalysts much more stable (Fig. 3B and D).

The catalytic performances at various feed compositions were compared on the basis of carbon amounts converted into different products (Table 3). The amount of carbon transformed from  $\text{CH}_3\text{SH}$  into products (excepting DMS), like the amount of carbon incorporated into C1–C3, BTX and coke, are average values over the 17-h period. The carbon and sulfur balances range between 101 and 103%, and 96 and 100%, respectively.

As shown in Table 3, with a  $\text{CH}_3\text{SH}/\text{N}_2$  mixture, 126 mg of initial carbon was transformed into C1–C3 (67 mg, 52%), BTX (51 mg, 40%) and coke (11 mg, 7.7%). With a  $\text{CH}_3\text{SH}/\text{N}_2/\text{H}_2\text{O}$  feed, selectivity to BTX increases (52% of the initial C), while selectivity to coke (2.6%) in particular sharply declines. With  $\text{CH}_4$ -containing feeds, the selectivity to C1–C3 obviously cannot be calculated but when they were used, without water, high selectivity to BTX (50%) and coke (9.7%) were observed. When both  $\text{CH}_4$  and  $\text{H}_2\text{O}$  are present in the process, high selectivity to BTX (69%) and low selectivity to coke (3.2%) were obtained. Note that adding water to the methanol feed also resulted in lower amounts of coke being produced in the MTH process [16]. In a previous work, we have shown that after multiple regenerations with air, the H-ZSM-5 catalyst keeps its initial properties [6].

Selectivity and coke formation in organic reactions are known to be very sensitive to the zeolite structure and Si/Al ratio [11–14,17–19]. For this reason, we performed additional experiments using a  $\text{CH}_3\text{SH}/\text{CH}_4/\text{H}_2\text{O}$  mixture and three catalysts: H-ZSM-5 (Si/Al = 15), H-Y (Si/Al = 15) and H-ZSM-5(75) (Si/Al = 75). Data summarized in Table 3 show that H-Y is less active than H-ZSM-5, promoting the formation of coke (12% selectivity), but exhibiting lower selectivity to BTX (only 6%).



**Fig. 3.** Conversion of methylmercaptan vs. time on H-ZSM-5 at 823 K, for various feed compositions: (A)  $\text{CH}_3\text{SH}/\text{N}_2$ , (B)  $\text{CH}_3\text{SH}/\text{H}_2\text{O}/\text{N}_2$ , (C)  $\text{CH}_3\text{SH}/\text{CH}_4/\text{N}_2$ , and (D)  $\text{CH}_3\text{SH}/\text{CH}_4/\text{H}_2\text{O}$ ; (●) conversion, (□)  $\text{H}_2\text{S}$ , (◇) DMS, (○)  $\text{CH}_4$ , (▽)  $\text{C}_2\text{H}_6$ , (Δ) BTX.

The behavior of H-ZSM-5 ( $\text{Si}/\text{Al}=75$ ) attracts more attention, though it is less active than H-ZSM-5 ( $\text{Si}/\text{Al}=15$ ). These two catalysts transformed respectively 89 and 125 mg carbon from  $\text{CH}_3\text{SH}$ . The selectivity to coke formation of H-ZSM-5(75) (2.7% vs. 3.2%) as well as the BTX selectivity (12% vs. 69%) are lower. A selectivity of ca. 85% to C1–C3 may be anticipated on H-ZSM-5(75).

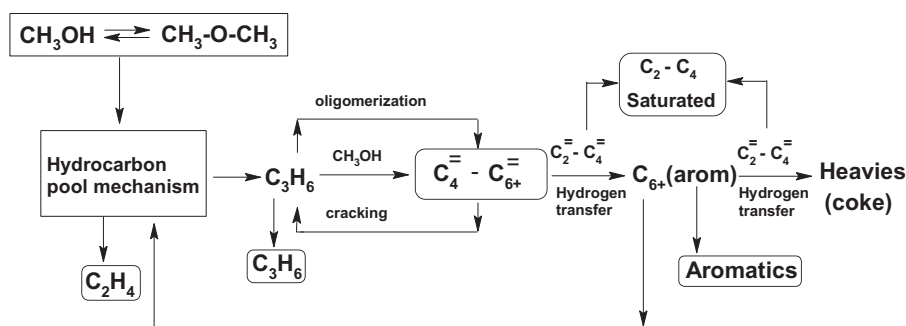
#### 4. Discussion

As pointed out in the introduction, only very few data about the catalytic conversion of methylmercaptan on protonic zeolites can be found in open literature. In contrast, hundreds of studies have addressed methanol transformation into hydrocarbons. Different aspects of the MTH process, including catalysts, kinetics and reaction mechanisms, have been widely discussed. A survey of the literature allows us to propose an overall reaction pathway (Scheme 2), which shows how the main classes of hydrocarbons ( $\text{C}_2$ – $\text{C}_6$  olefins, light alkanes and aromatics) can be obtained from methanol. There is general consensus that methanol is first dehydrated to dimethyl ether (DME), after which the equilibrium mixture formed is converted into hydrocarbons. The primary hydrocarbons are most probably lower olefins like ethylene and propylene. Their formation is supported by the so called “hydrocarbon pool” (HP) mechanism [15,20,21]. According to this assumption, the aromatic hydrocarbon pool species trapped within the pore/cages of zeolites undergo successive methylation steps by methanol and/or dimethyl ether (probably via surface methoxy species [22]), and eliminate further light olefins. The HP mechanism, requiring large cages and pores for accommodating the polymethylbenzene molecules, is strongly controlled by the texture

of the zeolites. The primary hydrocarbons from the HP cycle, particularly propylene, can easily be involved in further acid-catalyzed transformations, such as methylation and oligomerization, leading to the formation of  $\text{C}_4$ ,  $\text{C}_5$  and  $\text{C}_6+$  olefins. The  $\text{C}_6+$  species then play a part in either cracking processes (to form propylene and butenes) or in hydrogen transfer reactions (with light olefins) leading to the formation of aromatics and heavy carbonaceous products, simultaneously with the formation of saturated light hydrocarbons. Generally, the secondary reactions of the primary olefin products strongly depend on the process parameters (contact time, temperature and pressure) and the catalytic material (topology, density and strength of acid sites) [23,24]. Thus, short residence time, low temperature and low acid site density favor primary reactions to  $\text{C}_2$ – $\text{C}_6+$  olefins. Long residence time, high pressure and temperature, and high acid site density favor secondary reactions to aromatics, light alkanes and coke. The influence of zeolite topology is more complex. For instance: (i) H-SAPO-34 (2D system of narrow pores  $3.8 \times 3.8 \text{ \AA}$  connecting cages) favors ethylene and propylene; (ii) H-ZSM-5 (2D system of medium-size pores  $5.3 \times 5.6 \text{ \AA}$ ) is by far the most selective to aromatics and the least to producing coke; (iii) H-Y and H-BEA (3D system of large pores  $7\text{--}8 \text{ \AA}$ ) produce significant amounts of coke and light alkanes; this is particularly true for H-Y with long catalyst life-times which yielded only coke and  $\text{CH}_4$  [13].

With regard to the activity in MT2H (conversion of  $\text{CH}_3\text{SH}$  to final products, Table 2), the behavior decreases in the following order: H-ZSM-5 > H-Y > H-BEA > H-FER > H-MOR > H-SAPO-34. Generally, in the MTH process, the activity correlates with the number and strength of the acid sites. The number of acid sites was evaluated from the TPD of  $\text{NH}_3$  whose high temperature peak value





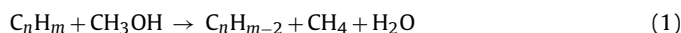
**Scheme 2.** Simplified representation of the different methanol conversion pathways over zeolites.

also gives information about their strength (Table 1 and Fig. S1). Data about the acidity of the commercial zeolites are also available in the open literature. For example, the ratios between the Bronsted and Lewis sites for H-ZSM-5, H-MOR, H-Y and H-BEA are 2.7, 4.1, 3.0 and 1.1, respectively [25]. All these data and results prove that there is no evident correlation between either the number/nature or the strength of acid sites and the activity of the catalysts. Under the present reaction conditions, it seems that the activity of H-zeolites in the M2TH process is not dominated by the acidity of the zeolite, rather that the zeolite topology is of utmost importance. Nevertheless, H-ZSM-5 is the most active and stable catalyst as in MTH.

Based on the experimental results, a number of similarities clearly exist between M2TH and MTH concerning the selectivity to aromatics and coke, but major differences appear in the selectivity to olefins and paraffins. Effectively, H-ZSM-5 produces a significant amount of aromatics and only a small quantity of coke in both processes. The first C–C bonds in the aliphatic molecules are probably formed by self-reactions of methoxy groups adsorbed on the zeolite surface [22]. Most likely, the one-ring aromatics come from the dehydrocyclization of alkanes/olefins containing 6–8 carbon atoms at least. The spatial constraints in H-ZSM-5 (pore size of about 5.5 Å, without cages) suppress the formation of polyaromatics which are precursors for coke formation. In contrast, large aromatic molecules can easily be formed and retained in the wide cages/pores of H-Y and H-BEA zeolites, which are the ones in which the largest amounts of coke were obtained (Table 2).

The absence of olefin and presence of C1–C3 alkanes (>94% CH<sub>4</sub>) greatly differentiate M2TH and MTH. This is true whatever the catalyst and even at lower temperatures (673–723 K, not reported here). In a recent article, Schultz [13] studied the elemental reactions of zeolite deactivation in the MTH process. Accordingly, the reactions can be divided into two groups – reactions of methanol with hydrocarbons/coke and reactions of hydrocarbons with one another. Among methanol reactions, a distinction is made between methylation and dehydrogenation. The methylation of olefins and

aromatics is the central step in the hydrocarbon-pool mechanism. Dehydrogenation with methanol proceeds via hydride transfer (Eq. (1)), leading to polyenes from olefins, to aromatics from cycloalkenes and to higher aromaticity of “coke” species, methane being the indicative co-product of this reaction (Eq. (1): C<sub>n</sub>H<sub>m</sub> refers aliphatic, aromatic or coke species).



Methanol is known to be an efficient alkylating agent, and methylation is therefore much more present in the MTH process than dehydrogenation. There is however nothing in literature to show that methylmercaptan is capable of methylating olefins/aromatics. Consequently, in the case of the M2TH process, dehydrogenation is the main reaction and results in the formation of aromatics, methane and coke (according to Eq. (1), where CH<sub>3</sub>SH and H<sub>2</sub>S replace CH<sub>3</sub>OH and H<sub>2</sub>O, respectively). It can further be stated that the hydrocarbon pool cycle (based on methylation steps, Scheme 2) is less sustained in M2TH than in MTH, a behavior that might explain the absence of light olefins in the M2TH product.

As previously reported for MTH [13,26], methane formation is one of the fingerprints of coke building. Our results in MTH (Figure 2) corroborate this assumption. As soon as dimethylether appears after 45 h on stream (obvious proof of deactivated catalyst), the formation of methane increases very fast at the expense of all other products. We assume that in this last period, hydrogen transfer occurs between coke and methanol to methane, and a coke of higher aromaticity prevails.

By analogy with MTH, we suggest that, in M2TH, a hydrogen transfer reaction between CH<sub>3</sub>SH and cycloalkanes/cycloalkenes bound to coke occurs, yielding CH<sub>4</sub>, H<sub>2</sub>S and coke of higher aromaticity. H-Y and H-BEA are effectively observed to yield the largest amounts of coke, to be far more selective to CH<sub>4</sub> than to BTX, with a molar ratio C1–C3/BTX of 50 when this ratio is about 6 on H-ZSM-5.

In a real M2TH process, methane will be the gas used to strip the adsorption bed (pre-concentration step) before the catalytic

**Table 1**  
Some characteristics of the catalysts.

Catalysts	Si/Al	Main pore size and system <sup>a</sup> (Å)	Surface <sub>BET</sub> (m <sup>2</sup> g <sup>−1</sup> )	Micropore volume (mL g <sup>−1</sup> )	Acid sites <sup>b</sup> (mmol g <sup>−1</sup> )
H-SAPO-34	–	3.8 × 3.8, 2D	640	0.251	1.03
H-ZSM-5	15	5.3 × 5.6, 2D	430	0.123	1.31
H-FER	10	5.4 × 4.2, 1D	360	0.131	1.82
H-MOR	10	6.5 × 7.0, 1D	530	0.188	1.81
H-Y	15	7.4 × 7.4, 3D	800	0.238	0.89
H-BEA	12.5	6.6 × 7.7, 3D	640	0.177	1.08

<sup>a</sup> Pore network system: 1D, unidirectional; 2D, bi-directional; 3D, tri-directional; from Atlas of zeolite structures [http://www.iza-structure.org/default.htm].

<sup>b</sup> The number of acid sites was determined from the amount of NH<sub>3</sub> desorbed in TPD experiments.

**Table 2**  
Catalyst behavior of zeolites in methyl mercaptan decomposition at 823 K over 6 h (5000 ppmv CH<sub>3</sub>SH in N<sub>2</sub>).

Catalyst	CH <sub>3</sub> SH conversion <sup>a</sup> (%)	Product composition (ppm)				Wt. loss <sup>d</sup> (mg)
		C1–C3 <sup>b</sup>	BTX <sup>c</sup>	H <sub>2</sub> S	DMS	
H-SAPO-34	73	750	20	2520	1120	5
H-ZSM-5	>99	2500	420	4850	0	4
H-FER	86	950	20	3020	820	7
H-MOR	76	810	20	2700	1090	9
H-Y	90	2120	40	3930	280	9
H-BEA	83	1580	25	3780	360	15

<sup>a</sup> Average value over 6 h

<sup>b</sup> CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub> in equivalent CH<sub>4</sub>.

<sup>c</sup> Benzene + toluene + xylene in equivalent benzene.

<sup>d</sup> Weight loss from TGA of the used catalyst.

**Table 3**CH<sub>3</sub>SH conversion on H-ZSM-5(15), H-ZSM-5(75) and H-Y at 823 K and 17 h to, at various feed compositions.

Catalyst	Feed composition <sup>a</sup>	CH <sub>3</sub> SH conv. (over 17 h)		DMS <sup>c</sup> (ppm)	C in gas products <sup>d</sup> (mg)		Wt. loss <sup>e</sup> (mg)	Chem. Anal. <sup>f</sup>		Selectivities to products <sup>g</sup> (%)		
		Average (%)	C <sup>b</sup> (mg)		C1–C3	BTX		C (mg)	S (mg)	C1–C3	BTX	“coke”
H-ZSM-5(15)	CH <sub>3</sub> SH/N <sub>2</sub>	95.0	126	85	67	51	11.0	9.7	2.2	52	40	7.7
H-ZSM-5(15)	CH <sub>3</sub> SH/H <sub>2</sub> O/N <sub>2</sub>	93.5	124	75	58	67	3.5	3.2	0.7	45	52	2.6
H-ZSM-5(15)	CH <sub>3</sub> SH/CH <sub>4</sub> /N <sub>2</sub>	87.0	98	320	– <sup>h</sup>	49	11.2	9.5	1.0	–	50	9.7
H-ZSM-5(15)	CH <sub>3</sub> SH/CH <sub>4</sub> /H <sub>2</sub> O	93.0	125	80	– <sup>h</sup>	88	5.5	4.0	0.6	–	69	3.2
H-ZSM-5(75)	CH <sub>3</sub> SH/CH <sub>4</sub> /H <sub>2</sub> O	89.0	89	500	– <sup>h</sup>	11	2.5	–	–	–	12	2.7
H-Y	CH <sub>3</sub> SH/CH <sub>4</sub> /H <sub>2</sub> O	82.0	79	500	– <sup>h</sup>	5	9.5	–	–	–	6	12

<sup>a</sup> CH<sub>3</sub>SH/N<sub>2</sub> (0.5/99.5), CH<sub>3</sub>SH/H<sub>2</sub>O/N<sub>2</sub> (0.5/2.0/97.5), CH<sub>3</sub>SH/CH<sub>4</sub>/N<sub>2</sub> (0.5/90.0/9.5), CH<sub>3</sub>SH/CH<sub>4</sub>/H<sub>2</sub>O (0.5/97.5/2.0)<sup>b</sup> Carbon from CH<sub>3</sub>SH converted into products, excepting DMS<sup>c</sup> DMS in the product mixture, average value<sup>d</sup> Carbon contained into the final products: C1–C3, BTX and “coke”.<sup>e</sup> Weight loss from TGA of the used catalyst<sup>f</sup> C and S contents in the used catalysts, from chemical analysis<sup>g</sup> The selectivity to products is defined as: (carbon in products)/(carbon converted from CH<sub>3</sub>SH) × 100.<sup>h</sup> Not evaluated owing to the presence of methane.

transformation of CH<sub>3</sub>SH takes place, and water might be present. Fig. 3 and Table 3 present the data of CH<sub>3</sub>SH conversion on H-ZSM-5 in these conditions.

In a dry CH<sub>4</sub> feed (CH<sub>3</sub>SH/CH<sub>4</sub>/N<sub>2</sub>), the lifetime of the catalyst is shorter and the selectivity to coke formation increases from 7.6% (without CH<sub>4</sub>) to 11.5% (Table 3). More aromatics are also formed. In a blank experiment, we have shown that CH<sub>4</sub> is inactive to yield coke and the catalyst remains white for the 20-h reaction. One possible explanation would be a reaction between coke or its precursors, formed in the course of M2TH, and an activated form of methane. In a wet feed without CH<sub>4</sub> (CH<sub>3</sub>SH/H<sub>2</sub>O/N<sub>2</sub>), the lifetime is longer and the selectivity to coke decreases from 7.6 to 2.5%; more aromatics are also formed. Marchi and Froment [16] have effectively shown that increasing the water content in the feed of the MTH process lowers the coke production rate. This was explained by a competitive chemisorption between water and coke precursors on strong acid sites. The steam reforming of coke to carbon oxides and hydrogen can also be considered as a coke scavenger.

Finally, when CH<sub>3</sub>SH is processed in the presence of both CH<sub>4</sub> and H<sub>2</sub>O (CH<sub>3</sub>SH/CH<sub>4</sub>/H<sub>2</sub>O), the lifetime remains long owing to the presence of water, though the presence of CH<sub>4</sub> increases the selectivity to coke from 2.5 to 4.4%, for the same reasons as discussed above (Table 3).

Water also decreases the selectivity to coke on H-Y (Table 3), which nevertheless remains much less active than H-ZSM-5, for a comparable number of acid sites, 0.89 and 1.21 mmol g<sup>−1</sup>, respectively.

In the MTH process, it has been demonstrated that the full reaction path obeys a consecutive scheme, in which aromatics and coke are terminal products (Scheme 2) [11,13,15,17,23]. The selectivity to these products strongly depends on the contact time and the progress of the transformation. As suggested by Janssens [27], the change in the active site number (Si/Al ratio or catalyst deactivation) is equivalent to modifying the contact time, and consequently, the reactions occurring in Scheme 2. According to our results, it is likely that the M2TH process also involves a complex reaction pathway, and the reasoning for MTH may thus be valid for M2TH too. For example, when two ZSM-5 samples with very different Si/Al ratio were compared, H-ZSM-5(75) was found to exhibit lower activity and selectivity to aromatics and coke than H-ZSM-5 (Tables 1 and 3). This behavior can be attributed to the large difference in acid site number: 0.27 and 1.21 mmol g<sup>−1</sup> for H-ZSM-5(75) and H-ZSM-5, respectively. The lower density of the acid sites in H-ZSM-5(75) is able to catalyze only certain reactions in a complex reaction scheme. Similar behavior can be observed in the case of H-ZSM-5(15) after its deactivation (Fig. 3). The selectivity to BTX decreases with the time-on-stream, suggesting that on a

deactivated catalyst (with a lower number of acid sites) the formation of aromatics is less favored.

## 5. Conclusions

These experimental results clearly demonstrate that the conversion of CH<sub>3</sub>SH into H<sub>2</sub>S and hydrocarbons can be successfully achieved at 823 K in the presence of protonic zeolites. Zeolite H-ZSM-5, with MFI topology showed the highest activity and deactivation stability. Over this catalyst, using dry CH<sub>3</sub>SH feeds, with either N<sub>2</sub> or CH<sub>4</sub> carrier gas, the lifetime was about 9 h and the amount of coke was 7.6–11.5%. When 2% of water was added to the gas feed, the catalyst lifetime was higher than 17 h (CH<sub>3</sub>SH conversion 95%) and the selectivity to coke decreased to 2.5–4.4%.

The conversion of methanol over H-ZSM-5 was investigated in order to compare M2TH and MTH. Although there are similarities between the two processes, significant differences, essentially regarding the product formation and distribution, were demonstrated. The HP mechanism seems to be less sustained in the case of M2TH process.

Finally, we consider that the valuable results reported in this study could be useful for developing a viable process for removing mercaptans from natural gas. The selective catalytic conversion of mercaptans into H<sub>2</sub>S and hydrocarbons over acid solid catalysts could be incorporated as a stage into an integrated system, including the adsorption/desorption of sulfur compounds on molecular sieves, mercaptan conversion over zeolites and H<sub>2</sub>S removal by absorption in basic solution.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.07.056>.

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